

1                   **HOMOGENEOUS MODIFIED-ALUMINA**  
2                   **FISCHER-TROPSCH CATALYST SUPPORTS**

3  
4                   FIELD OF THE INVENTION

5  
6       This invention relates to improved catalyst supports. More specifically, this  
7       invention relates to a homogeneous, amorphous modified-alumina cogel  
8       material, the attributes of which make it especially useful for use as a support  
9       for Fischer-Tropsch catalysts.

10  
11                  BACKGROUND OF THE INVENTION

12  
13       The preparation of hydrocarbons from synthesis gas is well known in the art  
14       and is usually referred to as Fischer-Tropsch synthesis, the Fischer-Tropsch  
15       process, or Fischer-Tropsch reaction(s). Catalysts for use in such synthesis  
16       usually contain a catalytically active Group VIII metal supported on a carrier.  
17       The support may be alumina, silica, titania, zirconia, magnesia and their  
18       mixtures. The Group VIII metals, iron, cobalt, nickel, and ruthenium have been  
19       often used as the catalytically active metals. Cobalt and iron have been found  
20       to be most suitable for catalyzing a process in which synthesis gas is  
21       converted to primarily hydrocarbons having five or more carbon atoms.  
22       Additionally, the catalysts often contain one or more promoters. The catalyst  
23       promoter may be a basic oxide such as ThO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub>, and TiO<sub>2</sub>,  
24       although promoters may also comprise noble metals such as Pt, Pd, Ru, Rh,  
25       Os, and Ir; coinage metals such as Cu, Ag, and Au; and other transition  
26       metals such as Fe, Mn, Ni, and Re. Fischer-Tropsch catalysts and processes  
27       are described in U.S. Patent Nos. 6,476,085; 6,586,481; and 4,568,663. The  
28       active metal may be incorporated into the base by impregnation, drying and  
29       calcination as disclosed in U.S. Patent Application 2003/0162849 A1 to van  
30       Berge et al.

31  
32       Alumina is one of the most desirable supports in catalysis. Due to its high  
33       surface area and good mechanical properties, particularly gamma form of

1 alumina has been used widely in industry for many catalytic applications.  
2 However, in an acidic or alcohol containing reaction medium such as  
3 Fischer-Tropsch synthesis conditions to produce wax, or other reactions  
4 proceeding in aqueous medium such as alcohol, ether, and ester syntheses,  
5 an alumina support exhibits a stability problem. Alumina may dissolve or leach  
6 slowly in the reactor due to attacks of acid and alcohol byproducts in the  
7 reaction medium. Dissolution of alumina support in acid medium is expected  
8 to be detrimental in catalyst stability. The dissolution problem may cause poor  
9 maintenance of catalyst integrity and possible fines generation. Possible fines  
10 generation will hurt the subsequent filtration and post processing operations.  
11 High metal or metal compound content in a Fischer-Tropsch product is  
12 undesirable because such contaminants could have adverse effects for the  
13 Fischer-Tropsch process, such as causing reactor plugging or significantly  
14 reducing catalyst life. As a result, it is important that the product of the  
15 Fischer-Tropsch process be free of metal and other contaminants that could  
16 adversely affect its subsequent processing.  
17  
18 Thus it is highly desirable to have a catalyst support with the favorable  
19 characteristics of an alumina support with much improved acid resistance.  
20  
21 U.S. Patent No. 5,733,839 to van Berge et al. shows that silica coating on  
22 gamma alumina particles improves dissolution tendency of alumina and the  
23 silica-coated alumina support is useful as a Fischer-Tropsch synthesis  
24 catalyst. U.S. Patent Application 2003/0162849 A1 to van Berge et al. shows  
25 that silica-coated alumina prepared via *in situ* coating in a slurry of aluminum  
26 hydroxylate prior to spray drying is also useful as a support for a  
27 Fischer-Tropsch synthesis catalyst. Daniell et al. studied the latter material in  
28 depth using FT-IR and XPS and showed that little mixing of the two oxide  
29 phases take place on the surface so the surface can be depicted as  
30 comprising two separate oxide phases (Applied Catalysis A: 196, 247-260,  
31 2000).

## SUMMARY OF THE INVENTION

This invention relates to a homogeneous, amorphous catalyst support comprising a modifying-metal-oxide and a base-metal oxide, in which the modifying-metal-oxide is homogeneously distributed throughout the base-metal oxide, the catalyst support having a Surface to Bulk modifying-metal /base-metal atomic ratio of from about 0.6 to about 1.3 and exhibiting an X-ray diffraction having broader line width and lower intensity than is exhibited by the base-metal oxide. More specifically, the present invention relates to a homogeneous, amorphous silica-modified-alumina catalyst support having a Surface to Bulk Si/Al ratio of from about 0.6 to about 1.3 and exhibiting an X-ray diffraction having broader line width and lower intensity than is exhibited by unmodified alumina. A silica-modified-alumina catalyst support of the present invention maintains the desirable properties of alumina and exhibits higher resistance to acid than unmodified alumina.

## BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a Powder X-ray diffraction of alumina and silica-modified alumina.

Figure 2 is a graph showing conductivity change as a function of time.

## DETAILED DESCRIPTION

The following detailed description is made with reference to a preferred embodiment of the invention, a silica-modified alumina Fischer-Tropsch catalyst support. It is not the intention that the invention be construed in this limited fashion. Other metal oxides may be used as support materials. For example, the base-metal oxides may be alumina, silica, titania and their mixtures. The base-metal oxides may be modified with modifying-metal-oxides such as silica, titania, zirconia, magnesia and their mixtures. The materials described may be used as a catalyst support for

1 catalysts other than Fischer-Tropsch catalysts. Other variations will be  
2 apparent to the skilled artisan base on the description herein.

3  
4 As more fully described herein, an acid resistant alumina support is prepared  
5 by cogellation of a homogeneous solution containing alumina and a small  
6 amount of silica. Upon calcination, the process produces gamma-type  
7 amorphous alumina with silicon dioxide incorporated uniformly throughout the  
8 structure. Aluminum leaching of this catalyst by acid attack is significantly  
9 reduced in this homogeneous silica-modified alumina support. This type of  
10 support may show advantages over the silica-coated alumina support when  
11 the reaction conditions are vigorous and cause attrition of catalyst particles. A  
12 silica-coated alumina support may lose its coating upon attrition in a reactor,  
13 whereas a catalyst support in accordance with the present invention will  
14 maintain its acid resistance uniformly throughout.

15  
16 As noted previously, the base support may be composed of alumina, silica,  
17 titania, magnesia and their mixtures. Alumina is the preferred base-metal  
18 oxide. Where the base support is alumina, the alumina component may have  
19 any phase form selected from eta, gamma, delta, theta, alpha and their  
20 mixtures, it is preferred that the base support is alumina in the gamma phase.  
21 The base material in the support is generally present in concentrations of from  
22 about 70 wt% or greater. Desirable base support content is from about  
23 70 - 99.75 wt% of base-metal oxide, preferably 80 - 99.5 wt%, and most  
24 preferably 90 - 99 wt%.

25  
26 Silica is the preferred modifier for alumina. Alternative modifiers can be titania,  
27 zirconia, magnesia, and mixtures thereof. Desirable modifier content is from  
28 about 0.25 - 30 wt% of modified oxide, preferably 0.5 - 20 wt%, and most  
29 preferably 1 - 10 wt%. The modified-alumina composition of the present  
30 invention is homogeneous. This means that silicon dioxide is incorporated  
31 uniformly throughout the structure of the particles. Two different indicators are  
32 described that demonstrate that silicon dioxide incorporation is uniform and  
33 that the composition is homogeneous.

1 First, a “Surface to Bulk Si/Al Ratio” (SB Ratio) is a measure used to indicate  
2 that the modified-alumina of the present invention is homogeneous.

3  
4  
5 SB Ratio = 
$$\frac{(\text{Si/Al atomic ratio of the } \textit{surface} \text{ measured by XPS})}{(\text{Si/Al atomic ratio of the } \textit{bulk} \text{ measured by elemental analysis})}$$
  
6  
7  
8

9 To determine the SB ratio, the Si/Al atomic ratio of the silica-modified alumina  
10 surface is measured using x-ray photoelectron spectroscopy (XPS). XPS is  
11 also known as electron spectroscopy for chemical analysis (ESCA). Since the  
12 penetration depth of XPS is less than 50 Å, the Si/Al atomic ratio measured by  
13 XPS is for the surface chemical composition. Use of XPS for silica-alumina  
14 characterization was published by W. Daniell et al. in Applied Catalysis A,  
15 **196**, 2000, pp 247-260. The XPS technique is, therefore, effective in  
16 measuring the chemical composition of the outer layer of catalytic particle  
17 surface. Other surface measurement techniques, such as Auger electron  
18 spectroscopy (AES) and Secondary ion mass spectroscopy (SIMS), could  
19 also be used for measurement of the surface composition.

20  
21 Separately, the bulk Si/Al ratio of the composition is determined from  
22 ICP elemental analysis. Then, by comparing the surface Si/Al ratio to the bulk  
23 Si/Al ratio, the SB ratio and the homogeneity of the material is determined.  
24 How the SB ratio defines the homogeneity of a particle is explained as  
25 follows. An SB ratio of 1.0 means the material is completely homogeneous  
26 throughout the particles. An SB ratio of less than 1.0 means the particle  
27 surface is enriched with aluminum (or depleted with silicon), and aluminum is  
28 predominantly located on the external surface of the particles. The SB ratio of  
29 more than 1.0 means the particle surface is enriched with silicon (or depleted  
30 with aluminum), and aluminum is predominantly located on the internal area  
31 of the particles.

1 A silica-modified-alumina composition is homogeneous when its Surface to  
2 Bulk ratio (SB ratio), i.e., the ratio of the Si/Al atomic ratio of the composition  
3 measured by XPS at the surface and the Si/Al atomic ratio of the bulk  
4 measured by elemental analysis is from about 0.6 to about 1.3. The SB ratio  
5 is preferably from about 0.8 to about 1.2, more preferably from about 0.9 to  
6 about 1.1, and most preferably 1.0.

7  
8 A second indicator of the homogeneity of the silica-modified-alumina of the  
9 present invention is the breadth of the linewidth of the X-Ray Diffraction  
10 peaks. As will be seen in the Examples, the linewidth of each or the XRD  
11 peaks is significantly broader for the silica-modified-alumina as compared to a  
12 reference unmodified alumina. For example, the full-width-at-half-height  
13 (FWHH) of the 38.5 degree  $2\theta$  peak, showed a linewidth that was increased  
14 by 113% compared to the reference alumina.

15  
16 In addition to being homogeneous, the silica-modified-alumina compositions  
17 of the present invention are amorphous, having a lower relative crystallinity  
18 than the reference unmodified alumina. The amorphous nature of the  
19 compositions of the present invention is shown by comparing the X-ray  
20 diffraction patterns of modified and unmodified compositions. As will be seen  
21 further in the Examples, the silica-modified-alumina has an overall intensity  
22 substantially lower than the reference alumina, which indicates that is more  
23 amorphous than the reference. In one instance, the relative crystallinity was  
24 estimated to be 58% of the reference by integrating the 38.5 degree  $2\theta$  peak.

25  
26 Silica-modified-alumina according to the present invention is preferably  
27 prepared by a cogel process. It may be prepared by a variety of methods  
28 employing batch and continuous processes in different combinations. The  
29 silica-modified-alumina is preferably prepared in accordance with the methods  
30 disclosed in commonly assigned U.S. Patent Application Serial  
31 No. 10/291,114 titled "Method for Preparing A Highly Homogenous  
32 Amorphous Silica-Alumina Composition", filed November 8, 2002 and  
33 incorporated by reference herein.

1 The two most important steps in the preparation of a silica-modified alumina  
2 cogel are (1) preparation of the clear sol containing silica and alumina and  
3 (2) gellation of the sol using a base solution. See U.S. Patent No. 4,289,653,  
4 Jaffe and U.S. Patent No. 4,988,659, Pecoraro, both of which are  
5 incorporated by reference herein.

6  
7 The starting materials for the sol preparation step include aluminum salt, acid,  
8 and a silica source. The aluminum salt source that can be used for the  
9 synthesis includes aluminum sulfate, aluminum nitrate, aluminum chloride,  
10 aluminum bromide, aluminum iodide, aluminum acetate, aluminum alkoxide,  
11 aluminum carboxylate, and aluminum metal or alumina dissolved in acid.  
12 Feasible acid sources include acetic acid, formic acid, sulfuric acid,  
13 hydrochloric acid, and nitric acid. The silicate sources include, but are not  
14 limited to, sodium silicate, precipitated silica dissolved in a base, and colloidal  
15 silica.

16  
17 The sol preparation can be done either via a batch process or a continuous  
18 process. It is critical to maintain the pH less than 3.0, preferably less than  
19 2.5, and to ensure vigorous and complete mixing of the aluminum salt and  
20 silicate solutions to minimize any unwanted gel or particle formation.

21  
22 A basic precipitant such as ammonium hydroxide is then added to the  
23 acidified sol solution. The addition of the precipitant raises the pH of the sol  
24 above 3, resulting in cogelling the silica and alumina species. Dilute ammonia  
25 solution is the preferred base for the gellation. In addition to dilute ammonia,  
26 other bases such as NaOH, NaAlO<sub>2</sub>, KOH or organic amine derivatives can  
27 also be used for the gellation. It is preferable to use an inorganic base for its  
28 lower cost.

29  
30 The gellation step can be done either via batch process or continuous  
31 process. The desirable final gellation pH is in the range of 5-9, preferably 6-8.  
32 It is critical to have complete, vigorous mixing of the Si-Al solution with the  
33 basic precipitant, and to maintain uniform pH throughout the mixture during

1 the precipitant addition step in order to minimize formation of isolated silica  
2 domains and alumina domains.  
3  
4 The precipitated cogel needs to be washed to remove any unreacted silicate  
5 and aluminum salt, and then it is ammonium exchanged to remove sodium.  
6 The cogel should be aged for approximately 2-5 hours at room temperature or  
7 at an elevated temperature of up to about 90°C and the aged cogel may be  
8 spray-dried for convenience in handling and storage, or for preparation of  
9 support for fluidized bed catalyst. The wet cake may be further processed to  
10 the final catalyst from the moist state.  
11  
12 The preferred method of drying and calcining of spherical form of supports  
13 includes an initial spray drying step in an air-purged dryer at 260-450°C and a  
14 final calcination at 480-850°C for 0.5-12 hours in a furnace or kiln.  
15  
16  
17 If desired, the material may be extruded to produce a fixed-bed catalyst or  
18 catalyst support. The silica-modified alumina as-is or in combination with other  
19 ingredients can be formed by adding sufficient amount of water to produce a  
20 moisture content of approximately 60% by weight. After mulling for  
21 approximately 1 hour, optionally in the presence of peptizing acid or base, the  
22 material will attain a plastic or doughy state which is suitable for extrusion in  
23 commercial extrusion apparatus. The extrudates then needs to be dried and  
24 calcined. The preferred method of drying and calcining includes an initial  
25 drying step in an air-purged oven at 65-175°C and a final calcination at  
26 480-850°C for 0.5-12 hours in a furnace or kiln. These and other methods of  
27 finishing the material are set forth in U.S. Patent No. 4,289,653, Jaffe,  
28 incorporated by reference herein.



## Examples

The following Examples are illustrative of the present invention, but are not intended to limit the invention in any way beyond what is contained in the claims which follow.

### Example 1: Synthesis of Silica-Modified-Alumina (2.5% SiO<sub>2</sub>/ 97.5% Al<sub>2</sub>O<sub>3</sub>)

An acidic aluminum solution (Solution I containing 10 wt% Al<sub>2</sub>O<sub>3</sub>) was prepared by dissolving 2309 g of AlCl<sub>3</sub>·6H<sub>2</sub>O and 13.7 g of hydrochloric acid (37% concentrated) in 2553 g of deionized water. A dilute solution of sodium silicate (Solution II containing 0.30 wt% SiO<sub>2</sub>) was prepared by diluting 43.6 g of concentrated sodium silicate solution (contains 29 wt% SiO<sub>2</sub> and 9% Na<sub>2</sub>O) with deionized water. The alumina/ hydrochloric acid solution (Solution I) and the silicate solution (Solution II) were pumped separately and simultaneously into the mixing chamber of an in-line blender. Mixing in the in-line blender was vigorous with 1600 RPM blender-blade rotation. The volume of the mixing chamber is smaller than the total volume of solutions pumped in 1 minute (i.e., less than 1 minute residence time per volume). The mixing produced a clear silica and alumina solution at the outlet of the inline blender (Solution III). The pH of the Solution III ranged 1.5 - 1.7. The Solution III contained

Si/Al atomic ratio of 0.022

H<sup>+</sup>/ Na<sup>+</sup> molar ratio of 1.1

Then the product from the in-line blender (Solution III containing the silica and alumina sol) and the dilute ammonia solution (Solution IV containing 8 wt% NH<sub>3</sub>) were pumped separately and simultaneously into the mixing chamber of a second in-line blender for gel formation. The rate of the ammonia solution was adjusted to maintain the pH of the gel product at 7 ± 0.5. The mixing in the in-line blender was again vigorous with 1600 RPM blender-blade rotation. The gel product was collected and then aged at room temperature for 2 hours while stirring. This cogelled silica-modified alumina was filtered to produce a

1 filtered cake. The cake was washed with deionized water followed by an  
2 ammonium exchange with a hot solution of ammonium nitrate (8.3 wt%, 24 L  
3 solution) for 15 minutes, and then rinsed with 48 L of deionized water. The  
4 final cake was dried at 250°F overnight. The silica-modified alumina was sized  
5 to small pieces and calcined under excess dry air at 1000°F for 1 hour for  
6 activation. Another sample was calcined at 1200°F for 1 hour to produce  
7 material with different porosity. Physical properties of the final silica-modified  
8 alumina are summarized in Table 1.

9  
10 Example 2: Synthesis of Silica-Modified Alumina (5% SiO<sub>2</sub>/ 95% Al<sub>2</sub>O<sub>3</sub>)

11  
12 The preparation procedure of this silica-modified alumina was similar to  
13 Example 1. The concentrations of Solution I and Solution II are modified to  
14 produce a combined solution of silica and alumina to a composition of

15  
16 Si/Al atomic ratio of 0.045

17 H<sup>+</sup>/ Na<sup>+</sup> molar ratio of 1.1

18  
19 Then the product from the in-line blender (Solution III containing the silica and  
20 alumina sol) and the dilute ammonia solution (Solution IV containing 8 wt%  
21 NH<sub>3</sub>) were pumped separately and simultaneously into the mixing chamber of  
22 a second in-line blender for gel formation. Then the gel product was purified  
23 via ammonium exchange and deionized water rinse. Physical properties of the  
24 final silica-modified alumina are summarized in Table 1.

1 Example 3: Synthesis of Silica-Modified Alumina (10% SiO<sub>2</sub>/ 90% Al<sub>2</sub>O<sub>3</sub>)

2  
3 The preparation procedure of this-silica-modified alumina was similar to  
4 Example 1. The concentrations of Solution I and Solution II are modified to  
5 produce a combined solution of silica and alumina to a composition of

6  
7 Si/Al atomic ratio of 0.094

8 H<sup>+</sup>/ Na<sup>+</sup> molar ratio of 1.1

9  
10 Then the product from the in-line blender (Solution III containing the silica and  
11 alumina sol) and the dilute ammonia solution (Solution IV containing 8 wt%  
12 NH<sub>3</sub>) were pumped separately and simultaneously into the mixing chamber of  
13 a second in-line blender for gel formation. Then the gel product was purified  
14 via ammonium exchange and deionized water rinse. Physical properties of the  
15 final silica-modified alumina are summarized in Table 1.

16  
17 Example 4: Commercial Alumina base case (100% Al<sub>2</sub>O<sub>3</sub>, non-invention)

18  
19 Physical properties of commercial pseudoboehmite alumina (Catapal B from  
20 Sasol Condea) were compared with the present silica-modified alumina. The  
21 pseudoboehmite alumina was calcined under excess dry air at 1000°F for  
22 1 hour to convert to the gamma -form of alumina. Another sample was  
23 calcined at 1200°F for 1 hour to produce gamma alumina with different  
24 porosity. Physical properties of the final gamma alumina are summarized in  
25 Table 1.

**Table 1**

Physical Properties and Conversion Activity  
of Silica-Modified Alumina Compositions

	<i>Reference, Gamma Alumina</i>	Silica-Modified Alumina Invention ( <i>Example 1</i> )	Silica-Modified Alumina Invention ( <i>Example 2</i> )	Silica-Modified Alumina Invention ( <i>Example 3</i> )
Nominal SiO <sub>2</sub> Content, wt%	0	2.5	5	10
<u>Porosity after 1000°F calcinations</u>				
Surface area, m <sup>2</sup> /g	293	338	365	412
Total pore volume, cc/g	0.43	0.47	0.44	0.58
<u>Porosity after 1200 °F calcinations</u>				
Surface area, m <sup>2</sup> /g	217	293	318	378
Total pore volume, cc/g	0.51	0.48	0.46	0.58
Na, wt%	-	<0.05	<0.05	<0.05
Bulk Si/Al atomic ratio, by elemental anal.	0	0.020	0.041	0.093
Surface Si/Al atomic ratio, by XPS	-	0.013	0.031	0.075
Surface to Bulk Si/Al Ratio	-	0.64	0.75	0.80
XRD, % crystalline alumina phase (38.5° 2θ peak)	100 % (base)	72 %	58 %	59 %
XRD, % linewidth (38.5° 2θ peak)	100 % (base)	163 %	213 %	244 %
<u>nC<sub>6</sub> + iC<sub>6</sub> Model Compound Testing (a)</u>				
Total conversion, wt%	3.1	-	4.7	3.9
nC <sub>6</sub> conversion, wt%	2.0	-	2.3	1.8
iC <sub>6</sub> conversion, wt%	4.1	-	7.1	5.9
Isopropylamine TPAD, mmol/g	base	-	Lower than the base	-

(a) Model compound testing was performed at 950°F, 0.68 WHSV of the combined hydrocarbon feed.

The present silica-modified alumina shows excellent physical properties as shown in Table 1. The silica-modified alumina samples show comparable or

1 higher surface area and pore volume than the reference alumina. The present  
2 silica-modified alumina shows better resistance to heat treatment in that it  
3 maintains the surface area better.

4  
5 The bulk Si/Al ratios of the silica-modified alumina samples in Table 1 are  
6 nearly identical to the compositions of the synthesis medium (Solution III,  
7 combined solution of silica and alumina). This indicates that silica  
8 incorporation is stoichiometric, nearly complete incorporation of silica into the  
9 alumina structure. The surface Si/Al ratios measured by XPS show  
10 comparable values to the bulk Si/Al ratios. The surface-to-bulk Si/Al ratios are  
11 close to 1 indicating the Si distribution in the material is uniform and  
12 homogeneous.

13  
14 Figure 1 compares the powder X-ray diffraction (XRD) pattern of commercial  
15 pseudoboehmite alumina to the present homogeneous silica-modified alumina  
16 (5 wt% SiO<sub>2</sub> case, Example 2) in dried-only form. The present silica-modified  
17 alumina exhibits two distinct characteristics. First, the overall intensity of the  
18 X-ray diffraction of the silica-modified-alumina is substantially less than the  
19 reference alumina indicating more amorphous nature of the material. By  
20 integrating the 38.5 degree 2 $\theta$  peak, it has an estimated 58% relative  
21 crystallinity compared to the reference alumina. Secondly, the linewidth of  
22 each XRD peaks are significantly broader, more than twice, than the  
23 reference alumina. By measuring the full-width-at-half-height (FWHH) of the  
24 38.5 degree 2 $\theta$  peak, it is determined that the linewidth was increased by  
25 113% compared to the reference alumina. The other silica-modified alumina  
26 samples exhibit the exact same behavior as reported in Table 1. The features  
27 of lower relative crystallinity and broader linewidth indicate that the present  
28 silica-modified alumina is very homogeneous in nature and the domain size of  
29 the alumina crystallites is significantly smaller than the reference alumina  
30 (much less than 100 Å).

31  
32 All silica-modified-alumina samples showed desirable low activity for  
33 hydrocarbon conversion as shown with the model compound testing.

1 Example 2 showed 4.7% total hydrocarbon conversion and  
2 Example 3 showed 3.9% conversion, comparable to the reference alumina  
3 sample with 3.1% conversion. Temperature programmed amine desorption  
4 study also shows that the support acidity of the present silica-modified  
5 alumina is comparable to or lower than that of reference gamma alumina. Low  
6 acidity of the support is desirable for metal catalyzed reactions where severe  
7 isomerization and cracking are undesirable, such as Fischer-Tropsch wax  
8 synthesis conditions.

9  
10 Example 5: Acid Resistance Test

11  
12 A method to obtain cumulative aluminum ion dissolution profile was disclosed  
13 U.S. Patent No. 5,733,839 to van Berge et al. in that concentration of  
14 aluminum ions was estimated using conductivity measurements at a constant  
15 pH as a function of time.

16  
17 In the present case, behavior of a support in an acid medium was evaluated  
18 by observing a conductivity change in the acid medium using a procedure  
19 similar to that disclosed by van Berge et al. For this experiment, 2 g of a  
20 support sample, which was calcined earlier at 1350°F for 1 hour, was slurried  
21 in a dilute nitric acid solution. Then the conductivity change was monitored for  
22 50 - 60 hours while maintaining the slurry pH at 2.0 using an automatic  
23 titrator. The conductivity change ( $\Delta$ ) is due to aluminum dissolution to form  
24  $Al^{3+}$  and other charged particles in the slurry. Thus the higher conductivity  
25 indicates higher dissolution tendency of the support. The conductivity change  
26 is plotted as a function time in Figure 2. The figure clearly indicates that  
27 silica-modified alumina shows much lower conductivity increase than pure  
28 gamma alumina at constant acid consumption, demonstrating the present  
29 silica-modified alumina exhibits improved acid resistance.

30  
31 While not being bound by any particular theory, the acid resistance of the  
32 present homogeneous silica-modified-alumina support may come from very  
33 fine domain of alternating silica and alumina phases in the support. The close

1 chemical bonding may generate very effective binding sites for alumina and  
2 hydrolyzed aluminum species. Even the digested alumina in the acid medium  
3 (partially hydrolyzed colloidal alumina) will be attached to the support with the  
4 stronger binding force. As a result, the homogeneous silica-modified-alumina  
5 is expected to generate much lower content of "soluble" aluminum species in  
6 a catalysis process that contains aqueous medium.

7

8 There are numerous variations on the present invention which are possible in  
9 light of the teachings and supporting examples described herein. It is  
10 therefore understood that within the scope of the following claims, the  
11 invention may be practiced otherwise than as specifically described or  
12 exemplified herein.